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Analysis of Secondary Battery Materials Under Low-Humidity or Air-Protected Condition†

1. Introduction

The Battery-Materials Analysis & Evaluation Center of JFE Techno-Research Corporation (JFE-TEC) performs evaluations and analyses for clients who are developing batteries or battery materials, including lithium ion batteries. As a total solution for battery development, environment-controlled equipment and analytical techniques, for example, under an ultra-low dew point (low-humidity) environment or non-atmospheric exposure (air-protected) environment are essential for performing an integrated series of processes from battery prototyping to charge-discharge testing, disassembly inspection and various kinds of analyses. This article introduces the current status of environment-controlled analytical techniques available at the Center.

2. Construction of Low-Humidity/Air-Protected Facilities

2.1 Features of Lithium Ion Batteries

2.1.1 Necessity of environmental control

With lithium ion batteries, which are being developed as secondary cells, high voltage drive that enables electrolysis in an aqueous electrolyte is possible by utilizing an organic solvent electrolyte with redox resistance over a wide potential range, and high energy density can be realized. On the other hand, process control that excludes moisture and analysis in an environment that is not exposed to moisture or the atmosphere are considered essential. Furthermore, because $LiPF_6$, which is used in electrolytic salts, reacts readily with water, generating the toxic compound HF, and metallic Li, which reacts explosively with oxygen and water, is handled on a regular basis, strict humidity control and analytical techniques that do not expose specimens to the atmosphere are necessary[1)].

2.1.2 Trends in battery material analysis

In analysis of materials for lithium ion batteries and their state analysis, techniques which enable measurement under a non-atmospheric exposure (air-protected) environment have come to be strongly demanded.

As an example in which state analysis under an air-protected environment is essential, analysis of the solid electrolyte interface (SEI), which forms on the surface of anode materials after charging and discharging, may be mentioned. Although SEI control is considered to determine the life of a battery, many aspects concerning the structure of the SEI are unclear, and as a result, structural analysis of the SEI has become a critical issue. As one problem in analysis of the SEI, the anode of a battery contains large amounts of active lithium ions and reduction products after charging and discharging, and the state of the SEI will change if the specimen is exposed to the atmosphere. Therefore, analysis of the anode became possible for the first time by providing an air-protected specimen transport function for all specimen preparation, processing and analysis equipment (**Photo 1**). In the case of cross-sectional processing by a focused ion beam (FIB) under an ambient condition (exposure to the atmosphere), a fine structure having a size of approximately 10 μm precipitates and the surface loses its flatness, as can be seen in the scanning electron microscopy (SEM) image of the cross section after processing in Photo 1 (a). In contrast, when processing is performed under an air-protected condition, as shown in Photo 1 (b), the cross section is smooth.

On the other hand, in the development of new materials, although deterioration due to moisture is a remarkable disadvantage, research on high Ni type lithium oxide active materials, which are expected to realize higher capacities, is also advancing. Thus, in the analysis and evaluation of new materials in the future, it is thought that there will be an increasing number of cases

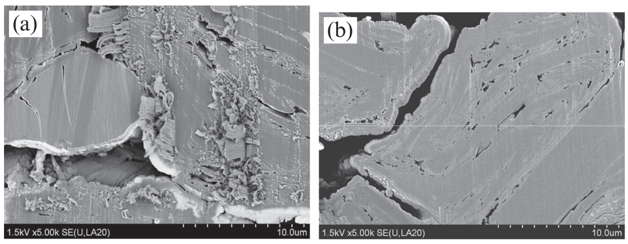

Photo 1 Scanning electron microscopic (SEM) images of anode cross-section fabricated under (a) ambient and (b) air-protected conditions

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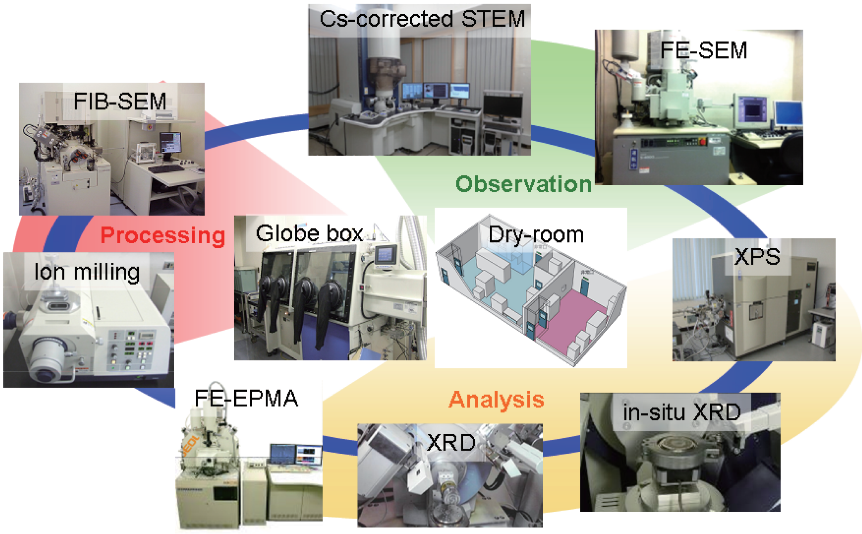

Cs-corrected STEM: Cs-Corrected scanning transmission electron microscope
FIB-SEM: Focused ion beam-Scanning electron microscope
FE-SEM: Field emission source-SEM
XPS: X-Ray photoemission spectrometer
FE-EPMA: FE-Electron probe micro-analyzer
XRD: X-Ray diffractometer

Fig. 1 Air-protected sample handling capable facilities network for analyzing battery materials

in which humidity control and environmental control techniques are critical.

2.2 Efforts for Low-Humidity and Air-Protected Analysis

Since the very beginning of the establishment of the JFE-TEC Battery-Materials Analysis & Evaluation Center, a group of air-protected facilities that ensure correct evaluation of battery materials have been accommodated, including the introduction of an air-protected ion milling system in November 2011. As of 2015, the Center possessed an argon glove box which enables operation at a dew point of −80°C or lower and an oxygen concentration of 1 ppm (volume concentration) or lower, and a dry room with a total floor area of 96 m^2, which includes a dry bench controlled by blowing air with a dew point of −85°C. The Center is constructing and expanding its air-protected specimen processing and analysis system with this equipment as a hub (**Fig. 1**).

As air-protected processing apparatuses, the Center has a specimen cross-section preparation apparatus using the above-mentioned argon ion milling and FIB. These apparatuses are also equipped with a cooling mechanism to prevent thermal damage during processing. Among air-protected specimen observation and analysis instruments, in addition to SEM and transmission electron microscopes (TEM), air-protection measures for a state-of-the-art spherical aberration corrected scanning transmission electron microscope (Cs-corrected scanning TEM) and X-ray photoemission spectrometer (XPS), Auger spectroscope, electron probe microanalyzer (EPMA), X-ray diffractometer (XRD) have already been completed. Analysis of crystallographic orientation by electron backscatter diffraction (EBSD) using SEM, and in-situ XRD analysis can also be performed under air-protected conditions.

Specimen pretreatment and specimen preparation under an air-protected environment or low dew point conditions using the Ar glove box and dry room are possible for high frequency inductively coupled plasma (ICP) analysis, nuclear magnetic resonance (NMR) analysis, gas chromatograph-mass spectroscopy (GC-MS) analysis, high performance liquid chromatography (HPLC) and chemical analysis by the Karl Fischer moisture meter.

Taking advantage of its large dry room, the Center has installed a full complement of equipment not only for analysis of batteries, but also for battery prototyping and disassembly work. The dry room is equipped with a continuous coater, roll press, automatic lamination device, ultrasonic welder, vacuum liquid injection device and other equipment for battery prototyping, and is controlled to the necessary dew point level for each process.

As an example of an analysis that was possible by utilizing this air-protected equipment, microstructural analysis of Si anodes, can be mentioned; this technology is also introduced in this issue of JFE Technical Report[2)]. This is a good example that could be realized because ion milling, FIB, TEM and SEM-EBSD observation and analysis were all possible under air-protected conditions.

3. Conclusion

Focusing on the keyword "low-humidity and air protected conditions," for the analysis of lithium ion batteries this article has introduced various advanced equipment at the JFE-TEC Battery-Materials Analysis & Evaluation Center.

Deterioration of materials due to handling in the atmospheric environment is not limited only to materials for lithium ion batteries, but also includes many other advanced materials which are under development in recent years. This also suggests the possibility of increasing need for air-protected environments in laboratories where those materials are developed. In the future, JFE Techno-Research Corporation will continue to promote advanced analytical systems to meet these needs.

References

1) e. g. The Committee of Battery Technology, Electrochem. Soc. J. Denchi Handbook. Ohmsha, 2010.
2) Simauchi, Y. et al. JFE Technical Report. 2017, no. 22, p. 55–59.

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